

# PATENT SPECIFICATION

(11) 1 464 427

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- (21) Application No. 15788/74 (22) Filed 10 April 1974
- (31) Convention Application No. 5458/73 (32) Filed 20 June 1973 (19)
- (31) Convention Application No. 8237/73 (32) Filed 25 Sept. 1973 in
- (33) Austria (OE)
- (44) Complete Specification published 16 Feb. 1977
- (51) INT CL<sup>2</sup> C11D 3/12
- (52) Index at acceptance

C5D 6A5B 6A5D2 6A5E 6A8B 6A9 6B10A 6B12B1 6B12E  
6B12G1 6B12G2A 6B12G4 6B12G6 6B12M 6B12N1  
6B1 6B2 6B9 6C6 6D



## (54) WASHING OR CLEANING COMPOSITIONS CONTAINING SILICATE CATION EXCHANGERS

(71) We, HENKEL & CIE. GMBH. a German Company, of 67 Henkelstrasse, Dusseldorf-Holthausen 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to washing or cleaning compositions.

The washing or cleaning compositions of the present time frequently contain relatively large amounts of condensed phosphates, especially tripolyphosphates, which are responsible for the good cleaning action of these compositions. The phosphate content of these agents has been criticised in publications in connection with the protection of the environment, the view being often held that this phosphate, arriving via the waste water into the rivers and lakes, leads to the nutritive properties of the waters, i.e. to an increase in the growth of algae and consumption of the oxygen. Attempts have therefore been made to remove or to substantially reduce the proportion of the phosphate present in washing and cleaning processes or in the compositions used therefor.

The washing compositions to be prepared according to the invention, which may contain little or no phosphate, are intended essentially for treatment of textiles, and the corresponding cleaning compositions are preferably intended for use in numerous other fields of technology and in the household for a wide variety of cleaning operations. Examples of such fields of application are the cleaning of appliances, apparatus, tubing and vessels of wood, plastic, metal, ceramics, glass and so on, in industry or in trade establishments, the cleaning of furniture, walls, floors, objects of ceramics, glass, metal, wood, plastic, the cleaning of polished or varnished surfaces in the household etc. Particularly important fields of application of the compositions prepared according to the invention are the washing and bleaching of textiles and the machine

cleaning of utensils of all kinds in industry, in professional laundries and in the household.

The present invention provides a process for the preparation of free flowing granules of a washing or cleaning composition comprising a finely divided, water-insoluble aluminium or boron silicate cation exchanger having the general formula



in which cat represents a cation of valency n exchangeable with calcium, x is a number from 0.7 to 1.5, Me represents boron or aluminium and y is a number from 0.8 to 6, preferably from 1.3 to 4, and having a calcium binding capacity of at least 50 mg CaO/g of anhydrous active substance (=AS), and a surfactant and/or builder substance wherein the silicate cation exchanger, moist from its preparation, is mixed with at least a part of the remaining constituents of the composition and this mixture is converted into free-flowing granules by removing the moisture from the silicate cation exchanger.

The calcium binding capacity of the above-defined compounds may reach values of 200 mg CaO/g AS and lies preferably in the range from 100 to 200 mg CaO/g AS.

Sodium is the preferred cation, but it may also be replaced by hydrogen, lithium, potassium, ammonium or magnesium as well as by the cations of water-soluble organic bases, for example by those of primary, secondary or tertiary amines or alkylamines with not more than 2 carbon atoms per alkyl residue or not more than 3 carbon atoms per alkylol residue.

For the sake of simplicity these compounds are denoted below as "aluminium silicates". Sodium aluminium silicates are preferably used. All information given for their preparation and processing obviously applies to the whole of the compounds defined above.

The aluminium silicates to be made according to the invention can be prepared

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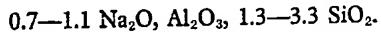
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synthetically in a simple way, by reaction of water-soluble silicates of an appropriate concentration with water-soluble aluminates of an appropriate concentration in the presence of water. For this purpose aqueous solutions of the water-soluble silicate and water-soluble aluminate may be mixed with one another or either the water-soluble silicate or the water-soluble aluminate in the solid state may be reacted with the aluminate or silicate respectively present as an aqueous solution. Also by mixing the silicate and aluminate present in the solid state the desired aluminium silicates are obtained in the presence of water, preferably with comminution of the mixture. Aluminium silicates can also be prepared from  $\text{Al(OH)}_3$ ,  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  by reaction with alkali metal silicate or aluminate solutions.

Of course, the cation-exchanging aluminium silicates to be used according to the invention are only formed by keeping to special precipitation conditions, since otherwise products are formed which have no cation-exchanging capacity or an insufficient cation exchanging capacity. The preparation of aluminium silicates utilisable according to the invention is described in the following preparations.

The aluminium silicates prepared by precipitation or converted by other processes into a finely divided state in aqueous suspensions can be converted by heating in the mother liquor at temperatures from 50° to 200°C from the amorphous into the aged or into the crystalline state. Although there is hardly any difference between the amorphous and the crystalline forms with respect to the calcium binding capacity, the crystalline aluminium silicates are preferably used for the purposes according to the invention. The preferred calcium binding capacity lying in the range of 100 to 200 mg  $\text{CaO}/\text{g AS}$  is found chiefly in compounds of the composition:



This combined formula includes two types of aluminium silicates which provided they are present in crystalline form, differ in their crystal structure and their X-ray diffraction diagram. These two types have the composition:

- (a)  $0.7-1.1 \text{ Na}_2\text{O}, \text{Al}_2\text{O}_3, 1.3-2.4 \text{ SiO}_2$
- (b)  $0.7-1.1 \text{ Na}_2\text{O}, \text{Al}_2\text{O}_3, >2.4-3.3 \text{ SiO}_2$

The still moist aluminium silicates obtained by one of the described processes, represent the starting material for the process according to the invention. This process enables the freshly precipitated, X-ray amorphous, finely divided aluminium silicates, aged in the moist

state or converted into the X-ray crystalline state, to be converted directly, i.e. without expensive separation and drying, into a free-flowing granular washing and cleaning composition. It is a special advantage of the process that the aluminium silicate particles substantially retain their degree of division determined by the conditions of preparation, while they agglomerate into larger structures if dried prior to incorporation into the compositions of the invention.

Aluminium silicates are preferably used of which at least 80% by weight have a particle size of 10 to  $0.01 \mu$ , preferably of 8 to  $0.1 \mu$ . Advantageously they should have no particles above  $40 \mu$ . In order to distinguish these finely divided aluminium silicates in this text from the coarser products, they are denoted as "microcrystalline", especially in the experimental part.

The aluminium silicates to be used according to the invention may be prepared essentially in the following states:

- (a) still flowable suspension of the aluminium silicate in the mother liquor, in which it is at the end of the process of preparation, the term "process of preparation" including any optional process, inclusive of a possible after-treatment, as for example, ageing or crystallisation, and in which case the mother liquor preferably does not contain any dissolved aluminium compounds,
- (b) Aluminium silicate, from which the mother liquor was partly separated,
- (c) obtained after partial or complete washing out of the mother liquor, a still flowable suspension of the aluminium silicate in water,
- (d) Aluminium silicate, from which the washing water was partly separated.

The form of aluminium silicates denoted by (b) and (c) chiefly includes viscous pastes, but also includes products still containing adhering water but already appearing powdery.

The mother liquor contains mostly surplus alkali metal hydroxides and/or alkali metal silicates, which during the further treatment of the aluminium silicates to produce the compositions of the invention can be converted into constituents of the said washing or cleaning compositions by neutralisation with acids or acid salts.

The acids or acid salts may be of inorganic nature, such as carbon dioxide, bicarbonates, sulphuric acid, bisulphates and other mineral acids. Organic acids, however, may also serve for this purpose, such as fatty acids or anionic surface-active substances in acid form. Substances which are not acid, but convertible into anionic surface-active substances by alkaline saponification are also useful, such as the  $\text{SO}_3^-$ -sulphonation products of olefines and the sulphoxidation or sulphochlorination products of alkanes. Acids utilisable in place of these are the complex-forming substances

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	or precipitation means for calcium (=builder substances) frequently used in washing compositions.	
5	A partial or complete separation of the mother liquor may be advantageous when either the mother liquor has to be returned to the preparation of the aluminium silicates, or when neutral to weakly alkaline reacting washing compositions are to be prepared.	70
10	The conversion of the moist aluminium silicates into free-flowing granular washing and cleaning compositions is possible in the main by two processes which are in principle:	75
15	1. A moist mixture of the aluminium silicates with at least a part of the other washing composition constituents is converted into free-flowing granules by drying.	80
20	2. The aluminium silicate in contact with water or mother liquor is mixed with substances which bind the water as water of hydration and/or crystallisation.	85
25	The first principle can be applied in practice by hot spraying or drying the water-containing mixture on hot surfaces.	90
30	In the case of the second process in principle there are several possibilities of putting this into practice. Starting from still flowable water-containing aluminium silicates, these can be sprayed on the moving solid constituents, which may be effected, for example, on moving plates, in rotating drums, in shovel or scoop arrangements and in fluidised beds. If the aluminium silicates are present as moist, but no longer flowable, powdery looking masses, it is often sufficient to mix them with the solid constituents of the washing or cleaning composition to be prepared, in order to obtain a granulated product.	95
35	The washing or cleaning composition according to the invention, in addition to the already mentioned surface-active substances and/or builder substances, may also contain the following constituents: non-surface-active foam stabilisers or inhibitors, textile softeners, chemically acting bleaching agents as well as stabilisers and/or activators for these, dirt carriers, corrosion inhibitors, antimicrobial substances, enzymes, brighteners, dyestuffs and perfumes etc. A few of these,	100
40	for example percompounds, active chlorine compounds and some enzymes, are unstable towards moisture and/or heat, so that they are usually admixed with the dry and cooled free-flowing granules. Oily or pasty constituents, such as non-ionic surface-active compounds, antimicrobial substances etc. are also frequently added later to the finished free-flowing granules.	105
45	Now follows an enumeration, classified according to groups of substances, of the possible constituents of the washing and cleaning compositions according to the invention.	110
50	The surface-active compounds contain in the molecule at least one hydrophobic organic residue and a water-solubilising anionic,	115
55	amphoteric or non-ionic group. The hydrophobic residue is usually an aliphatic hydrocarbon residue having 8 to 26, preferably 10 to 22, and especially 12 to 18 carbon atoms, or an alkylaromatic residue having 6 to 18, preferably 8 to 16 aliphatic carbon atoms.	120
60	Useful anionic surface-active compounds are, for example, soaps from natural or synthetic, preferably saturated fatty acids, in some cases also from resin or naphthenic acids. Suitable synthetic anionic surface-active substances are those of the sulphonate, sulphate and synthetic carboxylate type.	125
65	Suitable surface-active compounds of the sulphonate type are alkylbenzenesulphonates ( $C_6 - 15 - \text{alkyl}$ ), mixtures of alkene- and hydroxylalkane - sulphonates, as well as disulphonates, such as are obtained, for example, from monoolefines with a terminal or non-terminal double bond by sulphonation with gaseous sulphur trioxide and subsequent alkaline or acid hydrolysis of the sulphonation product. In addition alkanesulphonates, which are obtainable from alkanes by sulphochlorination or sulphoxidation and subsequent hydrolysis or neutralisation respectively or by bisulphite addition to olefines, are suitable. Further useful surface-active compounds of the sulphonate type are the esters of $\alpha$ - sulpho - fatty acids, for example the $\alpha$ - sulphinic acids from hydrogenated methyl or ethyl esters of coconut, palm kernel or tallow fatty acid.	130

in the alkyl residues, are particularly important. Besides these water-soluble nonionics, however, water-insoluble or not completely water-soluble polyglycolethers with 1 to 4 ethyleneglycoether residues in the molecule, are also of interest, especially when they are used together with water-soluble non-ionic or anionic surface-active compounds.

Further useful non-ionic surface-active compounds are the water-soluble addition products, containing 20 to 250 ethylene - glycoether groups and 10 to 100 propylene-glycoether groups, of ethylene oxide to polypropyleneglycol (=Pluronics (registered trade mark), alkylenediamine - polypropyleneglycol (=Tetronics (registered trade mark)) and alkylpolypropyleneglycols with 1 to 10 carbon atoms in the alkyl chain, in which the polypropyleneglycol chain functions as a hydrophobic residue.

Non-ionic surface-active compounds of the amine-oxide or sulphoxide type are also useful.

The foaming power of the surface-active compounds can be increased or reduced by combination of suitable types of surface-active compounds; a reduction can also be achieved by additions of non-surface-active organic substances.

Surface-active carboxy- or sulfo - betains, as well as the above-mentioned nonionics of the aikylolamide type are suitable as foam stabilisers, principally with surface-active compounds of the sulphonate or sulphate type; moreover fatty alcohols or higher terminal diols have also been proposed for this purpose.

A reduced foaming power, which is desirable when working in machines, is frequently obtained by combination of different types of surface-active compounds, for example, of sulphates and/or sulphonates with nonionics and/or with soaps. In the case of soaps the inhibition of foaming rises with the degree of saturation and the number of carbon atoms in the fatty acid residue; soaps of the saturated C<sub>20-24</sub> fatty acids are therefore specially suitable as foam inhibitors.

N - alkylated aminotriazines possibly containing chlorine, which are obtained by reaction of 1 mol of cyanuric chloride with 2 to 3 mol of a mono- and/or di - alkylamine with 6 to 20, preferably 8 to 18 carbon atoms in the alkyl residue are non-surface-active foam inhibitors. Propoxylated and/or butoxylated aminotriazines have a similar action, for example products which are obtained by addition of 5 to 10 mol of propylene oxide to 1 mol of melamine and further addition of 10 to 50 mol of butylene oxide to this propylene oxide derivative.

In addition, water-insoluble organic compounds such as paraffins or halogenated paraffins with melting points below 100°C, aliphatic C<sub>18</sub>- to C<sub>30</sub>-ketones, as well as aliphatic carboxylic acid esters which contain at least 18 carbon atoms in the acid or in the alcohol residue, possibly also in each of these two residues (for example triglycerides or fatty acid-fatty alcohol esters) are suitable as non-surface-active foam inhibitors; they can be used especially in combinations of surface-active compounds of the sulphate and/or sulphonate type with soaps for inhibiting the foam.

Particularly weakly foaming nonionics, which may be used both alone and in combination with anionic, amphoteric and non-ionic surface-active compounds, and which reduce the foaming power of strongly foaming surface-active compounds, are the products of addition of propylene oxide to the already mentioned surface-active polyethyleneglycolethers as well as the likewise already described products of addition of ethylene oxide to polypropyleneglycols and to alkylenediamine - polypropyleneglycols or to C<sub>1</sub> - 10 - alkyl - polypropyleneglycols.

Suitable builder substances are weakly acid, neutral or alkaline reacting inorganic or organic salts.

Such weakly acid, neutral or alkaline reacting salts utilisable according to the invention are, for example, the bicarbonates, carbonates, borates or silicates of the alkali metals, alkali metal sulphates, and the alkali metal salts of organic, non-surface-active sulphonic acids, carboxylic acids and sulphonocarboxylic acids containing 1 to 8 carbon atoms. These include, for example, water-soluble salts of benzene-, toluene- or xylene - sulphonic acid, water-soluble salts of sulphoacetic acid, sulphonbenzoic acid or sulphonocarboxylic acids.

Substances which exert a complex-forming and/or precipitating action on the calcium present in the water as the substance causing hardness are of particular importance as builder substances, especially in combination with the above-mentioned alkalis. Substances forming complexes with calcium with so small a complex-forming capacity that they have not hitherto been regarded as typical complex-forming substances for calcium, are also suitable for the purposes of the invention but such compounds often have the ability to retard the precipitation of calcium carbonate from aqueous solutions.

To the complex-forming or precipitating agents belong those of inorganic nature, for example, pyrophosphate, triphosphate, higher polyphosphates and metaphosphates.

The constituents of the products to be used preferably as textile washing agents or as domestic cleaning agents, especially the builder substances, are usually chosen so that the preparations have a neutral to strongly alkaline reaction, so that the pH value of a 1% solution of the preparation usually lies in the range from 7 to 12. Fine washing com-

positions, for example, have a mostly neutral to weakly alkaline reaction (pH value = 7 to 9.5), while soaking, prewashing and boiling washing compositions are adjusted so that they are more strongly alkaline (pH value = 9.5 to 12, preferably 10 to 11.5). If higher pH values are desired for special cleaning purposes, these can easily be adjusted by use of alkali metal silicates with a suitable  $\text{Na}_2\text{O} : \text{SiO}_3$  ratio or by alkali metal hydroxides.

Organic compounds, which serve as complex-forming or precipitating means for calcium, are found among the polycarboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, carboxyalkylethers, poly-anionic polymeric carboxylic acids and the phosphonic acids, these compounds being mostly used in the form of their water-soluble salts.

Examples of polycarboxylic acids are dicarboxylic acids of the general formula



with  $n=0$  to 8, besides maleic acid, methylenemalonic acid, citraconic acid, mesaconic acid, itaconic acid, non-cyclic polycarboxylic acids with at least 3 carboxyl groups in the molecule, as for example tricarballylic acid, aconitic acid, ethylenetetracarboxylic acid, 1,1,3,3 - propane - tetracarboxylic acid, 1,1,3,3,5,5 - pentane - hexacarboxylic acid, hexanehexacarboxylic acid, cyclic di- or poly - carboxylic acids, as for example cyclopentane - tetra - carboxylic acid, cyclohexane - hexacarboxylic acid, tetrahydrofuran - tetracarboxylic acid, phthalic acid, terephthalic acid, benzenetri, tetra- or penta - carboxylic acid as well as mellitic acid.

Examples of hydroxymono- or poly - carboxylic acids are glycollic acid, lactic acid, malic acid, tartronic acid, methyltartronic acid, gluconic acid, glyceric acid, citric acid, tartaric acid, or salicylic acid.

Examples of aminocarboxylic acids are glycine, glycylglycine, alanine, asparagine, glutamic acid, aminobenzoic acid, iminodi- or tri - acetic acid, hydroxyethyl - iminodiacetic acid, ethylene - diamino - tetraacetic acid, hydroxyethyl - ethylenediamino - triacetic acid, diethylenetriamino - pentaacetic acid as well as higher homologues, which may be prepared by polymerisation of an N - aziridylcarboxylic acid derivative, for example of acetic acid, succinic acid, tricarballylic acid, and subsequent saponification, or by condensation of polyamines with a molecular weight of 500 to 10,000 with chloroacetic acid or bromoacetic acid salts.

Examples of carboxyalkylethers are 2,2 - hydroxydisuccinic acid and other etherpolycarboxylic acids, especially polycarboxylic acids containing carboxymethylether groups, to which belong the corresponding derivatives

of the following polyhydric alcohols or hydroxycarboxylic acids, which may be completely or partly etherified with the glycollic acid: glyco, di- or tri - glycols, glycerine, di- or tri - glycerines, glycerinemonomethyl-ether, 2,2 - dihydroxymethylpropanol, 1,1,1 - trihydroxymethyl - ethane, 1,1,1 - trihydroxymethylpropane, erythritol, pentaerythritol, glycollic acid, lactic acid, tartronic acid, methyltartronic acid, glyceric acid, erythronic acid, malic acid, citric acid, tartaric acid, trihydroxyglutaric acid, saccharic acid or mucic acid.

As transition types to the polyanionic polymers the carboxymethylethers of sugar, starch and cellulose may be mentioned.

Among the polyanionic polymers the polymeric carboxylic acids play a special part, for example, polymers of acrylic acid, hydroxyacrylic acid, maleic acid, itaconic acid, mesaconic acid, aconitic acid, methylenemalonic acid, citraconic acid and the like, the copolymers of the above-mentioned carboxylic acids with one another or with ethylenically unsaturated compounds such as ethylene, propylene, isobutylene, vinyl alcohol, vinylmethylether, furan, acrolein, vinyl acetate, acrylamide, acrylonitrile, methacrylic acid, crotonic acid etc., as for example the 1:1 mixed polymer from maleic anhydride and ethylene or propylene or furan.

Further polyanionic polymers of the type of polyhydroxy - polycarboxylic acids or polyaldehydo - polycarboxylic acids are chiefly built up from acrylic acid- and acrolein units or acrylic acid and vinyl alcohol units, which are obtainable by copolymerisation of acrylic acid and acrolein or by polymerisation of acrolein and a subsequent Cannizzaro reaction, possibly in the presence of formaldehyde.

Examples of phosphorus-containing organic complex-forming compounds are alkanephosphonic acids, amino- and hydroxy - alkanephosphonic acids and phosphonocarboxylic acids, as for example the compounds methanediphosphonic acid, propane - 1,2,3 - triphosphonic acid, butane - 1,2,3,4 - tetraphosphonic acid, polyvinylphosphonic acid, 1 - aminoethane - 1,1 - diphosphonic acid, 1 - amino - 1 - phenyl - 1,1 - diphosphonic acid, aminotrimethylencetriphosphonic acid, methylamino- or ethylamino - dimethylenediphosphonic acid, ethylene - diaminotetramethylenetetraphosphonic acid, 1 - hydroxyethane - 1,1 - diphosphonic acid, phosphonoacetic acid, phosphonopropionic acid, 1 - phosphonoethane - 1,2 - dicarboxylic acid, 2 - phosphonopropane - 2,3 - dicarboxylic acid, 2 - phosphonobutane - 1,2,4 - tricarboxylic acid, 2 - phosphonobutane - 2,3,4 - tricarboxylic acid as well as mixed polymers from vinyl phosphonic acid and acrylic acid.

By the use of the above-described aluminium silicates according to the invention

5	it is directly possible to keep the content of the treatment baths at not more than 0.6 g/litre, preferably at not more than 0.3 g/litre of organically and/or inorganically bound phosphorus, even when phosphorus-containing inorganic or organic complex-forming or precipitating means for calcium are used. However, a good result can also be obtained on working without such phosphorus containing compounds.	benzamide, N - methyl - N - mesyl - p - nitro - benzamide, and N - methyl - N - mesyl - p - methoxybenzamide, N - acylated cyclic hydrazides, acylated triazoles or urazoles as, for example, monoacetylmaleic acid hydrazide, O,N,N - trisubstituted hydroxylamines as, for example, O - benzoyl - N,N - succinyl - hydroxylamine, O - acetyl - N,N - succinyl - hydroxylamine, O - p - methoxybenzoyl - N,N - succinyl - hydroxylamine, O - p - nitrobenzoyl - N,N - succinylhydroxylamine and O,N,N - triacetyl - hydroxylamine, N,N' - diacyl - sulphurylamide, as for example, N,N' - dimethyl - N,N' - diacetyl - sulphurylamide, and N,N' - diethyl - N,N' - dipropionyl - sulphurylamide, triacyl cyanurates for example triacetyl- or tribenzoyl cyanurate, carboxylic acid anhydrides, for example benzoic anhydride, m - chlorobenzoic anhydride, phthalic anhydride, 4 - chlorophthalic anhydride, sugar esters, as for example, glucosepentaacetate, 1,3 - diacyl - 4,5 - diacyloxy - imidazolidines, for example the compounds 1,3 - diformyl - 4,5 - diacetoxy - imidazolidine, 1,3 - diacetyl - 4,5 - diacetoxyl - imidazolidine, 1,3 - diacetyl - 4,5 - dipropionyloxy - imidazolidine, acylated glycolurils, as for example tetrapropionylglycoluril or diacetyl - dibenzoyl - glycoluril, diacylated 2,5 - diketopiperazines, as for example 1,4 - diacetyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 2,5 - diketopiperazine, 1,4 - dipropionyl - 3,6 - dimethyl - 2,5 - diketopiperazine, acetylation or benzoylation products of propylenediurea or 2,2 - dimethyl - propylenediurea (2,4,6,8 - tetraaza - bicyclo - (3,3,1) - nonane - 3,7 - dione or its 9,9 - dimethyl derivative), sodium salts of p - (ethoxycarbonyloxy) - benzoic acid and p - (propoxycarbonyloxy) - benzenesulphonic acid.	70
10	Among the compounds serving as bleaching agents which provide H <sub>2</sub> O <sub>2</sub> in water, sodium perborate tetrahydrate (NaBO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> , 3H <sub>2</sub> O) and the monohydrate (NaBO <sub>2</sub> , H <sub>2</sub> O <sub>2</sub> ) have special importance. Other H <sub>2</sub> O <sub>2</sub> -providing borates are useful, however, for example perborax Na <sub>2</sub> B <sub>2</sub> O <sub>7</sub> , 4H <sub>2</sub> O. These compounds may be partly or completely replaced by other active oxygen carriers, especially by peroxyhydrates, such as peroxycarbonates (Na <sub>2</sub> CO <sub>3</sub> , 1.5 H <sub>2</sub> O <sub>2</sub> ), peroxyphosphates, citrate perhydrates, urea-H <sub>2</sub> O <sub>2</sub> - or melamine-H <sub>2</sub> O <sub>2</sub> -compounds as well as by H <sub>2</sub> O <sub>2</sub> -yielding peracid salts, as for example, salts of Caro's acid (KHSO <sub>5</sub> ), perbenzoates or peroxyphthalates.	75	
15	It is advisable to incorporate the usual water - soluble and/or water - insoluble stabilisers for the peroxy-compounds together with these in amounts from 0.25 to 10% by weight. Suitable water-insoluble stabilisers which, for example, constitute 1 to 8, preferably 2 to 7% of the weight of the total preparation, are the magnesium silicates MgO : SiO <sub>2</sub> = 4:1 to 1:4, preferably 2:1 to 1:2 and especially 1:1, mostly obtained by precipitation from aqueous solutions. Other alkaline earth metal, cadmium or tin silicates of corresponding composition are utilisable in their place. Water-containing oxides of tin are also suitable as stabilisers. Water-soluble stabilisers, which may be present together with water-insoluble, are the organic complex-forming substances the amount of which may constitute 0.25 to 5, preferably 0.5 to 2.5% of the weight of the total preparation.	80	
20	In order to obtain a satisfactory bleaching action during the washing even at temperatures below 80°C, especially in the range from 60° to 40°C bleaching components containing activators are preferably incorporated in the preparations.	85	
25	As activators for percompounds yielding H <sub>2</sub> O <sub>2</sub> in water, serve certain N-acyl- and O-acyl-compounds forming with this H <sub>2</sub> O <sub>2</sub> organic per-acids, especially acetyl-, propionyl- or benzoyl compounds, as well as carbonic acid- or pyrocarbonic acid esters. Useful compounds are among others: N - diacylated and N,N' - tetraacylated amines as for example, N,N,N',N' - tetraacetyl - methylenediamine or -ethylenediamine, N,N - diacetyl aniline and N,N - diacetyl - p - toluidine or 1,3 - diacylated hydantoins, alkyl - N - sulphonyl - carbonamides, for example N - methyl - N - mesylacetamide, N - methyl - N - mesyl -	90	
30	The active chlorine compounds serving as bleaching agents may be inorganic or organic.	95	
35	The inorganic active chlorine compounds include alkali metal hypochlorites, which may be used especially in the form of their mixed salts or compounds of addition to orthophosphates or to condensed phosphates as for example, to pyro- and poly-phosphates or to alkali metal silicates. If the washing compositions and washing assistants contain monopersulphates and chlorides, active chlorine is formed in aqueous solution.	100	
40	Suitable organic active chlorine compounds are especially the N - chloro - compounds, in which one or two chlorine atoms are linked to a nitrogen atom, the third valency of the nitrogen atom leading to a negative group, especially to a CO— or SO <sub>2</sub> — group. Dichloro- and trichloro - cyanuric acids or their salts, chlorinated alkylguanides or alkylbiguanides, chlorinated hydantoins and chlorinated melamines belong to these compounds.	105	
45	Further, the preparations according to the	110	
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invention may contain dirt carriers, which keep the dirt detached from the fibres suspended in the liquor and thus prevent greying. Water-soluble colloids, usually organic, are suitable for this purpose, for example, the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ethercarboxylic acids or ethersulphonic acids of starch or cellulose or salts of acid sulphuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also suitable for this purpose. In addition, soluble starch preparations and starch products other than those mentioned above can be used, as for example, degraded starch, aldehyde starches and so on. Polyvinylpyrrolidone is also utilisable.

The enzyme preparations to be used are mostly a mixture of enzymes with different action, for example of proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerasases, lyases, transferases, desmolases or nucleases. The enzymes obtained from strains of bacteria or fungi such as *Bacillus subtilis* or *Streptomyces griseus* are of particular interest, especially proteases or amylases, which are relatively stable towards alkali, percompounds and anionic surface-active compounds and are still active at temperatures up to 70°C.

Enzyme preparations are put on the market by the manufacturers usually as aqueous solutions of the active substances or as powders, granulates or as cold sprayed products. They contain as diluents or blending agents frequently sodium sulphate, sodium chloride, alkali metal ortho-, pyro- or poly-phosphates, especially tripolyphosphates. Special value is placed on dust-free preparations; they are obtained in known way by incorporation of oily or pasty nonionics or by granulation by means of melts of salts in their own water of crystallisation.

Enzymes may be incorporated which are specific for a fixed type of dirt, for example proteases or amylases or lipases; combinations of enzymes of different action, especially combinations of proteases and amylases, are preferably used.

The washing compositions may contain as optical brighteners for cotton, especially derivatives of diaminostilbenedisulphonic acid or their alkali metal salts. For example, salts of 4,4' - bis - (2 - anilino - 4 - morpholino - 1,3,5 - triazine - 6 - yl - amino) - stilbene - 2,2' - disulphonic acid or similarly constructed compounds which contain a diethanolamino group, a methylamino group or a 2 - methoxyethylamino group instead of the morpholino group, are suitable. Brighteners for polyamide fibres are those of the type of 1,3 - diaryl - 2 - pyrazolines, for example the compound 1 - (p - sulphonamylphenyl) - 3 - (p - chlorophenyl) - 2 - pyrazoline as well as similarly constructed compounds which contain for example, the methoxycarbonyl, 2 - methoxyethoxycarbonyl, acetylarnino or vinylsulphonyl groups instead of the sulphonamyl group. Useful polyamide brighteners are also the substituted aminocoumarins, for example 4 - methyl - 7 - dimethylamino- or 4 - methyl - 7 - diethylamino - coumarin. Furthermore, the compounds 1 - (2 - benzimidazolyl) - 2 - (1 - hydroxyethyl - 2 - benzimidazolyl) - ethylene and 1 - ethyl - 3 - phenyl - 7 - diethylamino - carbostyryl are useful as polyamide brighteners. The compounds 2,5 - di - (2 - benzoxazolyl) - thiophene, 2 - (2 - benzoxazolyl) - naphtho[2,3 - b] - thiophene and 1,2 - di - (5 - methyl - 2 - benzoxazolyl) - ethylene are suitable as brighteners for polyester and polyamide fibres. In addition, brighteners of the type of the substituted 4,4' - distyryldiphenyl may be present; for example the compound 4,4' - bis(4 - chloro - 3 - sulphostyryl) - diphenyl. Mixtures of the above-mentioned brighteners may also be used.

The aluminium silicate content of the compositions to be prepared according to the invention may lie in the range from 5 to 95, preferably 15 to 60%.

The amount of inorganic phosphates and/or organic phosphorus compounds present in the compositions of the invention should preferably not be greater than corresponds to a total phosphorus content of the agent of 6%, preferably of 3%.

The compositions of typical textile washing compositions to be used at temperatures in the range from 50° to 100°C lies generally within the range of the following formulation:

- 5-30% anionic and/or non-ionic and/or amphoteric surface-active compounds
- 5-70% aluminium silicates
- 2-45% complex-forming compound for calcium
- 0-50% washing alkalis (=alkaline builder substances) not capable of forming complexes
- 0-50% bleaching agent as well as other added substances usually present in smaller amounts in textile washing agents.

In contrast to the washing of textiles, the machine cleaning of utensils, owing to the different kinds of materials to be cleaned and the different kinds of dirt, require the use of cleaning agents, the composition of which necessarily deviates from that of the textile washing agents.

As utensils within the meaning of the invention are meant all utensils or apparatus of ceramic material, glass, plastics, wood and metal used in the household, in trade and professional operations and in industry in preservation or storage, in the preparation and serving of foods and drinks, which are to be

cleaned after their use. The process according to the invention can thus be used, besides in the household and in restaurants or guest houses, also in large kitchen units, dairies, in the drinks industry, for example breweries, in factories processing or preparing lemonade, mineral water and fruit juices, for the machine washing and cleaning of utensils, especially bottles.

The cleaning compositions obtainable according to the invention are suitable also for washing laboratory apparatus and appliances, even when these are contaminated by residues other than food residues.

The aluminium silicates are preferably combined with alkaline-reacting substances, which are used in an amount such that the pH value of the treatment liquor lies in the range from 8 to 13. Such alkaline reacting substances are preferably alkali metal silicates and alkali metal carbonates, and, if higher pH values are wanted, alkali metal hydroxides.

The action of the cleaning compositions prepared according to the invention can be improved by addition of small amounts of surface-active compounds, especially non-ionic surface-active compounds. Moreover, an addition of oxidising substances, especially active chlorine compounds, in some cases also of percompounds has proved advantageous.

Typical compositions for the machine cleaning of utensils have the following formulation:

35	10—60% alkali metal silicates and/or carbonates and/or hydroxides and/or inorganic phosphorus-containing compounds forming complexes with calcium	100
40	10—65% aluminium silicates 0—40% other usual constituents of machine utensil-washing compositions	105
45	The following substances, which are usually present in the indicated amounts, belong to the other usual constituents of machine dishwashing compositions: 0—10% substances containing active chlorine or active oxygen 0—10% surface-active substances, especially non-ionic surface-active substances 0—20% sodium sulphate and/or water.	110
50	All these percentage data are weights per cent; in the case of the aluminium silicates they relate to the anhydrous active substance (=AS).	115
55	The synthesis of the moist aluminium silicates used for the preparation according to the invention of washing and cleaning compositions is described hereinafter but no protection therefor is here claimed.	120
60	For this purpose the aluminium silicate solution was treated in a 15-litre vessel with the sodium silicate solution with vigorous stirring (temperature of the solutions: 20—80°C). In an exothermic reaction an X-ray amorphous sodium aluminium silicate was thereby formed as the primary precipitation product. After 10 minutes vigorous stirring the suspension of the precipitated product was either directly, i.e. without crystallisation, further processed, or it was left at 80°C for 3 to 6 hours for the purpose of crystallisation. The products thus obtained were completely crystalline according to X-ray structural analysis.	70
65	In a variant of the process, the suspensions of the X-ray amorphous or crystalline primary particles (particle size 0.5—50, mostly 1—10 $\mu$ ) were used together with the mother liquor directly for the preparation of washing or cleaning compositions; in another variant the mother liquor was filtered off (Suction filter or screen centrifuge) and the still moist aluminium silicate powder, possibly washed out with deionised water, was processed.	75
	The contents of active substance (=AS) of the processed starting materials were obtained in the case of the suspensions by filtering off the mother liquor and washing out the filter residue until a pH value of 10 in the wash water was attained, and in the case of the moist powder by further washing in the described way, drying of the washed residues and heating of the dried residues at 800°C for one hour.	80
	In the preparation of microcrystalline aluminium silicates (characterised by the addition "m") the aluminate solution diluted with deionised water was mixed with the silicate solution and treated with a high-speed intensive stirrer (10,000 rpm; product "Ultraturrax" of the firm Janke und Kunkel IKA-Werk, Staufen/Breisgau/Federal Republic of Germany). After 10 minutes vigorous stirring the suspension of the amorphous precipitated product was transferred to a crystallisation vessel, where the formation of large crystals was prevented by stirring the suspension. After filtering off the liquor from the crystal slurry by suction and further washing with deionised water, until the washings running off had a pH value of about 10, the filter residue was dried, then ground in a ball mill and separated into two fractions in a centrifugal separator (Mikropex-Windsichter of the firm Alpine, Augsburg, Federal Republic of Germany), of which the finer fraction contained no fractions over 10 $\mu$ . The grain size distribution was determined by means of a sedimentation balance.	85
	The aluminium silicates obtained had the approximate composition (calculated on anhydrous products (=AS)):	95
	1 Na <sub>2</sub> O, 1 Al <sub>2</sub> O <sub>3</sub> , 2 SiO <sub>2</sub> .	100
	All quantity data (% or parts) relate to the weights.	105

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The calcium binding capacity of the aluminium silicates was determined in the following way: 1 litre of an aqueous solution containing 0.594 g of  $\text{CaCl}_2$  ( $=300 \text{ mg CaO/litre} = 30^\circ \text{ German hardness}$ ) and adjusted with dilute NaOH to a pH value of 10 was mixed with 1 g of aluminium silicate (referred to AS). Then the suspension was stirred vigorously for 15 minutes at a temperature of  $22^\circ\text{C}$  ( $\pm 2^\circ\text{C}$ ). After filtering off the aluminium silicate, the residual hardness  $x$  of the filtrate was determined. From this the calcium binding capacity was calculated in mg CaO/g AS according to the formula:

$$(30-x) \cdot 10$$

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#### Preparation conditions for the aluminium silicate suspension S1:

Precipitation:	8.450 kg aluminate solution of the composition 11.3% $\text{Na}_2\text{O}$ , 18.7% $\text{Al}_2\text{O}_3$ , 70.0% $\text{H}_2\text{O}$
	6.550 kg of a 34.9% sodium silicate solution of the composition 1 $\text{Na}_2\text{O}$ , 3.46 $\text{SiO}_2$
Further treatment:	none
$\text{Na}_2\text{O}$ excess:	0.55 kg = 3.7%
AS content:	4.25 kg = 28.3%
Calcium binding capacity:	120 mg CaO/g AS

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#### Preparation conditions for the aluminium silicate suspension S2:

Precipitation:	as under S1
Further treatment:	crystallisation
$\text{Na}_2\text{O}$ excess:	0.55 kg = 3.7%
AS content:	4.25 kg = 28.3%

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#### Preparation conditions for the aluminium silicate powder P1:

Precipitation:	as under S1
Further treatment:	no crystallisation, filtering by suction of the mother liquor, further washing with 10 litres of water
AS content:	4.25 kg = 34%
Calcium binding capacity:	120 mg CaO/g AS

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#### Preparation conditions for the aluminium silicate powder P2:

Precipitation:	as under S1
Further treatment:	crystallisation, filtering off with suction of the mother liquor, further washing with 10 litres of water
AS content:	4.25 kg = 55%
Calcium binding capacity:	170 mg CaO/g AS

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#### Preparation conditions for the aluminium silicate powder P3:

Precipitation:	as under S1
Further treatment:	crystallisation, centrifuging off of the mother liquor, further washing with 10 litres of water
AS content:	4.16 kg = 65%
Calcium binding capacity:	170 mg CaO/g AS

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55

Now follows the description of the preparation of some aluminium silicate suspensions, in which the excess  $\text{Na}_2\text{O}$  present in the mother liquor, was decomposed with  $\text{CO}_2$  or  $\text{NaHCO}_3$ , as a first step for the preparation of pulverent washing or cleaning agent.

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#### Preparation conditions for the aluminium silicate suspension S3:

Precipitation:	as under S1
Further treatment:	$\text{CO}_2$ was passed through the suspension until the calculated $\text{CO}_2$ -absorption (0.39 kg) was reached.

Na<sub>2</sub>CO<sub>3</sub> content: 0.94 kg=6.1%  
AS content: 4.25 kg=27.6%  
Calcium binding capacity: 120 mg CaO/g AS

Preparation conditions for the aluminium silicate suspension S4:

5      Precipitation: as under S1  
Further treatment: crystallisation, then passing in CO<sub>2</sub> as with  
aluminium silicate S3  
Na<sub>2</sub>CO<sub>3</sub> content: 0.94 kg=6.1%  
AS content: 4.25 kg=27.6%  
10     Calcium binding capacity: 170 mg CaO/g AS

Preparation conditions for the aluminium silicate suspension S5:

Precipitation: as under S1  
Further treatment: crystallisation, then 1.49 kg of NaHCO<sub>3</sub> were  
stirred into the suspension  
15     Na<sub>2</sub>CO<sub>3</sub> content: 1.88 kg=11.3%  
AS content: 4.25 kg=25.9%  
Calcium binding capacity: 170 mg CaO/g AS

Preparation conditions for the aluminium silicate suspension S2m:

20     Precipitation: as under S1 (modified to produce micro-  
crystals)  
Na<sub>2</sub>O excess: 0.55 kg=3.7%  
AS content: 4.25 kg=28.3%  
Calcium binding capacity: 175 mg CaO/g AS

Preparation conditions for the aluminium silicate powder P2m:

25     Precipitation: as under S1 (modified to produce micro-  
crystals)  
Further treatment: after the crystallisation, filtering off by suction  
of the mother liquor, further washing with  
10 litres of water  
30     AS content: 4.25 kg=55%  
Calcium binding capacity: 175 mg CaO/g AS

Preparation conditions for the aluminium silicate powder P3m:

Precipitation: as under S1 (modified to produce micro-  
crystals)  
35     Further treatment: after crystallisation, the mother liquor was  
centrifuged off, further washing with 10  
litres of water  
AS content: 4.16 kg=65%  
Calcium binding capacity: 175 mg CaO/g AS

40     Now follows the description of the preparation of some aluminium silicate suspensions, in  
which the excess Na<sub>2</sub>O in the mother liquor was reacted with CO<sub>2</sub> or NaHCO<sub>3</sub>, as a first  
step for the preparation of pulverulent washing or cleaning compositions.

Preparation conditions for the aluminium silicate suspension S4m:

45     Precipitation: as under S1 (modified to produce micro-  
crystals)  
Further treatment: after the crystallisation, CO<sub>2</sub> was passed in  
until the calculated CO<sub>2</sub> absorption  
(0.39 kg)  
50     Na<sub>2</sub>CO<sub>3</sub> content: 0.94 kg=6.1%  
AS content: 4.25 kg=27.6%  
Calcium binding capacity: 175 mg CaO/g AS

Preparation conditions for the aluminium silicate suspension S5m:

Precipitation:	as under S1 (modified to produce micro-crystals)
Further treatment:	after the crystallisation, stirring of 1.49 kg NaHCO <sub>3</sub> into the suspension
Na <sub>2</sub> CO <sub>3</sub> content:	1.88 kg = 11.3%
AS content:	4.25 kg = 25.9%
Calcium binding capacity:	175 mg CaO/g AS

The particle size distribution of the above described microcrystalline aluminium silicates determined by sedimentation analysis lay in the following range:

$$\begin{array}{ll} >40 \mu = 0\% & \text{Particle size maximum} = 1-3 \mu \\ <10 \mu = 100\% & \\ <8 \mu = 99\% & \end{array}$$

Examples

15 Now follows the description of the compositions according to the invention with use of the aluminium silicate suspensions or the moist aluminium silicate powder obtained as described above. The salt constituents of the washing or cleaning composition mentioned in the Examples (surface-active substances, other organic salts as well as inorganic salts) were present as sodium salts, if not expressly stated otherwise. The terms and abbreviations used have the following meaning:  
 20 "ABS" is the salt of an alkylbenzenesulphonic acid with 10 to 15, preferably 11 to 13 carbon atoms in the alkyl chain, and obtained by condensation of straight-chain  
 25 olefines with benzene and sulphonation of the alkylbenzene thus obtained.  
 30 "Soap" is prepared from a hardened mixture of equal parts by weight of tallow and rape oil fatty acids,  
 35 "OA+xEO" and "TA+xEO" are the products of addition of ethylene oxide (EO) to technical oleyl alcohol (OA) and to tallow

fatty alcohol (TA) (I.V. 0.5) respectively, while the figures for x represent the molar amount of ethylene oxide added on to 1 mol of alcohol.

40 The "nonionic" is an addition product of ethylene oxide to a polypropyleneglycoether of molecular weight 1900, obtainable under the trade name "Pluronic L 61", while the fraction of the polypropyleneglycoether constitutes 90% by weight and the fraction of the polyethyleneglycoether constitutes 10% by weight.

45 "Perborate" is a technical product of the approximate composition NaBO<sub>2</sub>, H<sub>2</sub>O, 3 H<sub>2</sub>O,

50 "Waterglass" is a 34.5% aqueous solution of the sodium silicate of composition Na<sub>2</sub>O, 3.35 SiO<sub>2</sub>,

55 "EDTA" is the salt of ethylenediaminetetraacetic acid,

"DCIC" is the sodium salt of dichloroisocyanuric acid,

60 "CMC" is the salt of carboxymethylcellulose.

Example 1

Pulverulent washing compositions of the formulation:

65 2.0% ABS	1.0% CMC
8.5% OA+10 EO	1.0% EDTA
7.0% Na <sub>2</sub> P <sub>5</sub> O <sub>10</sub>	40.0% aluminium silicate (AS)
19.0% Na <sub>2</sub> CO <sub>3</sub>	15.0% water
6.5% Na <sub>2</sub> SiO <sub>3</sub>	

70 were prepared using the above described aluminium silicate suspensions or powders according to the following process:

Process 1a

All the other constituents of the formulation were successively stirred into 140 kg of the aluminium silicate suspension S1 and then the excess alkali was converted into Na<sub>2</sub>CO<sub>3</sub> by reaction with 3.6 kg of gaseous CO<sub>2</sub>. The resulting aqueous slurry of washing constituents after hot spraying provided a flowable hollow ball powder.

75 80 When the aluminium silicate suspension

S2 was treated in the described way, similar results were obtained.

Process 1b

The aluminium silicate powder P1 was mixed with the ABS paste, diluted with the corresponding amount of water, and then further treated as described under 1a, of course without CO<sub>2</sub> treatment.

**Process 1c**

To carry out this process a mixer of the firm Lödige, Paderborn, Federal Republic of Germany, was used. This mixer consisted of a horizontal cylinder with a cooling jacket. The contents of the cylinder were thoroughly mixed by rotating arms provided with ploughshare-like vanes. After putting in the dry components of the formulation, the aluminium silicate powder P2 was intermixed and granulates were formed. Then the remaining constituents of the formulation were sprinkled in. The still somewhat moist granulate taken from the mixer was aerated to carry away the heat of hydration. A flowable granulate was obtained as end product.

If the aluminium silicate powder P3 is used in this process, the formation of granulate when the powder is mixed in is greatly reduced, owing to its lower water content; this does not take place until after addition of the remaining constituents of the formulation.

**Process 1d**

The operation is as under 1a, but the aluminium silicate suspension S3 or S4 is used. Since the neutralisation of the excess Na<sub>2</sub>O with CO<sub>2</sub> has already occurred in the suspension, the passing of CO<sub>2</sub> into the charge described under 1a is omitted.

If in this process the aluminium silicate suspension S5 is used (NaHCO<sub>3</sub> addition), correspondingly smaller amounts of Na<sub>2</sub>CO<sub>3</sub> are needed during the preparation of the aqueous batch.

**Process 1e**

The process described under 1c was altered inasmuch as a not washed out aluminium silicate powder P2 was treated by blowing CO<sub>2</sub> into the mixer with neutralisation of the excess Na<sub>2</sub>O still present in the aluminium silicate.

**Process 1f**

The process described under 1a was varied inasmuch as first of all the ABS was mixed as free acid with the aluminium silicate suspension S1 and then the remaining constituents of the formulation were added.

The powders prepared by the processes 1a to 1f, especially that prepared by hot spraying, can be converted into bleaching washing compositions by addition of 15 to 35% of perborate.

**Example 2**

For the preparation of a washing composition of formulation:

3.5% soap	3.0% waterglass
7.0% TA+10 EO	1.8% CMC
3.0% TA+5 EO	0.5% EDTA
15.0% aluminium silicate (AS)	2.5% MgSiO <sub>3</sub>
20.0% Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	5.0% Na <sub>2</sub> CO <sub>3</sub>
27.0% perborate	11.7% water

a mixture of the solid constituents with the exception of the soap and the perborate was granulated in a similar way to that described in Example 1c with admixture of a pasty mixture of the aluminium silicate powder P1, the waterglass, the soap and the two EO derivatives. If the aluminium silicate powders P2 or P3 containing little water are used, corresponding amounts of water are added. The perborate is intermixed after cooling the granulate.

If it is desired to remove the Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> still further or to eliminate it completely, it is suitably replaced by a mixture of 65% Na<sub>2</sub>CO<sub>3</sub> and 35% of citrate or 35% of O-carboxymethyl tartrate.

**Example 3**

For the preparation of a cleaner for domestic dish-washing machines of the composition:

35.0% aluminium silicate (AS)	80
35.0% Na <sub>2</sub> SiO <sub>3</sub>	
1.0% DCIC	85
10.0% nonionic	
5.0% waterglass	
14.0% water	

the operation is carried out in the mixer according to Example 1c. Aluminium silicate powder P3, say half the powdered Na<sub>2</sub>SiO<sub>3</sub> and the nonionic are introduced. The waterglass is sprayed on this moving powder mixture and the remaining Na<sub>2</sub>SiO<sub>3</sub> as well as the DCIC are added. A stream of air is passed through the primary granulate in the mixer, which causes a part of the introduced water to evaporate.

**Example 4**

For the preparation of a cleaner containing 100 sodium hydroxide of the composition:

35.0% aluminium silicate (AS)	100
11.0% Na <sub>2</sub> SiO <sub>3</sub>	
15.0% Na <sub>2</sub> CO <sub>3</sub>	
4.0% DCIC	105
11.0% NaOH	
6.0% waterglass	
18.0% water	

the operation is effected with use of one of the aluminium silicate suspensions S1 or S2 after addition of NaOH in a similar way to that described in Example 3.

If in Examples 1 and 2 the ABS and the soap are replaced by other anionic surface-active compounds, as for example olefine-sulphonates, alkanesulphonates or esters of  $\alpha$ -sulpho-fatty acids, similar results are obtained. In addition, the fatty alcohol-EO derivatives contained in the washing compositions according to Examples 1 and 2 can be partly or completely replaced by the said

5 anionic surface-active compounds; in all these cases, since soap reduces the foaming ability of synthetic anionic surfactants, if the soap is omitted, the foaming ability increases considerably. Therefore, the foaming ability of the washing composition can be adjusted by interchanging various anionic surfactants.

10 As the Examples show, the aluminium silicate can be directly converted into a free-flowing granular washing or cleaning composition without isolating it from the mother liquor or—in case the mother liquor has been wholly or partly separated—without drying it. For this reason the activity of the aluminium silicates in the washing or cleaning compositions obtainable according to the invention is in no way impaired.

15 The processes described in Examples 1 to 4 were also carried out with use of the following moist microcrystalline aluminium silicates:

in Example 1a: aluminium silicate suspension S2m

20 in Example 1c: aluminium silicate powder P2m

25 in Example 1d: aluminium silicate suspension S4m

If in this process the aluminium silicate suspension S5m is used (NaHCO<sub>3</sub> addition), correspondingly smaller amounts of Na<sub>2</sub>CO<sub>3</sub> are needed in the preparation of the aqueous batch.

30 in Example 1e: aluminium silicate powder P2m

35 in Example 1f: aluminium silicate suspension S2m

in Example 2 : aluminium silicate powder P2m—aluminium silicate powder P3m

40 in Example 3 : aluminium silicate powder P3m

45 in Example 4 : aluminium silicate suspension S2m

#### WHAT WE CLAIM IS:—

1. A process for the preparation of free-flowing granules of a washing or cleaning composition, comprising a finely divided, water-insoluble aluminium or boron silicate cation exchanger having the general formula:



50 in which cat represents a cation of valency n exchangeable with calcium, x is a number from 0.7 to 1.5, Me represents boron or aluminium and y is a number from 0.8 to 6 and having a calcium binding capacity of at least 50 mg CaO/g of anhydrous active substance (=AS) and a surfactant and/or builder substance, wherein the silicate cation exchanger moist from its preparation is mixed with at least a part of the remaining

constituents of the composition and the mixture is converted into free-flowing granules by removing the moisture from the silicate cation exchanger.

55 2. A process as claimed in claim 1 in which y is a number from 1.3 to 4.

3. A process as claimed in claim 1 or 2 in which the silicate cation exchanger is free from the mother liquor in which the compounds are formed on preparation.

70 4. A process as claimed in claims 1 or 2 in which the silicate cation exchanger is associated with the mother liquor, in which the compounds are formed on preparation, to give a pourable product.

75 5. A process as claimed in any one of claims 1, 2, and 4 in which said composition also comprises a conventional constituent of a washing or cleaning composition in the form of a salt produced by reaction of the excess alkali present in the said mother liquor with an acid.

80 6. A process as claimed in claim 5, in which an inorganic acid is used for the reaction with the excess alkali of the said mother liquor.

85 7. A process as claimed in claim 5, in which an organic acid is used for the reaction with the excess alkali of the said mother liquor.

90 8. A process as claimed in claim 5 or 7, in which an anionic surface-active compound in acid form is used for the reaction with the excess alkali of the said mother liquor.

95 9. A modification of the process as claimed in claim 5, in which a saponifiable pre-product of an anionic surface-active compound is used for the reaction with the excess alkali of the said mother liquor.

100 10. A process as claimed in claim 9 in which the saponifiable pre-product of the anionic surface-active compound is the sulphonation or sulphoxidation product of aliphatic hydrocarbon or a sulphonation product of an olefine.

105 11. A process as claimed in claim 5 or 7, in which acids, the salts of which are capable of forming complexes with calcium, are used for the reaction with the excess alkali of the said mother liquor.

110 12. A process as claimed in any one of claims 1 to 11 in which the moist silicate cation exchanger is converted into free-flowing granules by mixing with a salt which is able to bind the water as water of crystallisation.

115 13. A process as claimed in claim 12, in which the silicate cation exchanger of claim 1 is largely freed from the mother liquor, but is still moist prior to mixing with the salt.

120 14. A process as claimed in any one of claims 1 to 11 in which a mixture present as an aqueous slurry of the silicate cation exchanger mixed with at least a part of the remaining constituents of the composition as